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Effect of Heating Rate on Edible Mushroom Bran Pyrolysis

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Abstract

Pyrolysis characteristics of edible mushroom bran at heating rates of 10, 20, 30 K/min in a dynamic nitrogen flow of 20 ml/min were investigated applying a thermogravimetric analyzer(TG) coupled with a Fourier transform infrared (FTIR) spectrometer. Effects of heating rate on pyrolysis parameters and composition of pyrolysis vapor were studied. The results show that with the heating rate increasing, the starting temperature, final temperature of pyrolysis and the maximum rates of mass losses increased. Compared to the composition of pyrolysis vapour at the heating rate of 10K/min, molality of H₂O,CO₂,phenol,carboxylic compounds increase 61.6%, 3.6%, 36.4%, 13.0% at the heating rate of 20 K/min and 107.2%, 67.1%,40.7%,25.9% at the heating rate of 30 K/min, respectively. While molality of acids decrease 17.43% at the heating rate of 20 K/min and 75.30% at the heating rate of 30 K/min compared to that of at the heating rate of 10 K/min. The important difference is hydrocarbon was found amount in pyrolysis vapour at the heating rate of 10 K/min, but little at the heating rate of 20 K/min and 30 K/min.

Keywords: Edible mushroom bran; Pyrolysis; Heating rate; Product distribution

1. Introduction

Biomass is the most common form of renewable energy ^[1, 2]. Compared to the other forms of renewable energy such as solar energy, wind energy et al, biomass can be converted to liquid fuels directly ^[3–5]. Pyrolysis is proven to be one of the most promising technologies for liquid oil production, with solid char and gases as valuable by-products ^[6, 7]. However, oil production need a lot of biomass materials. Biomass species fall into two broad categories ^[8, 9]: one is various kinds of biomass materials from industrial production and agricultural residues; another is energy crops from artificial cultivation. Large amounts of energy crops planting will occupy cropland for large-scale biomass fuels production. Biomass from agricultural residue is distributed dispersedly in China and gathering them together will increase the cost of biomass utilization. Biomass materials from industrial production have advantage of huge quantity, concentrated distribution and local use of producing biomass fuels saves transportation cost. Commonly it is difficult to acquire suitable method to reuse industrial production waste, which is not only a waste of resources but also causes environmental pollution ^[10]. Therefore, industrial residues as biomass materials to produce oil are one of novel areas in biomass utilization. Unfortunately, there is still a lack of detailed theoretical study on pyrolysis of the residues.

In the paper, edible mushroom bran after mushroom cultivation process was chosen as the biomass

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material and the pyrolysis characteristic of it was investigated used TG-FTIR. The effect of heating rate on the pyrolysis parameters such as temperature and weight loss, composition of pyrolysis vapour was investigated.

2. Experiment

TG-FTIR analyzer is used to investigate the pyrolysis characteristics of the edible mushroom bran and pyrolysis vapour simultaneously. The sample powder mass of 8 mg were heated from room temperature (about 20 °C) to 800 °C at 10, 20, and 30 °C · min⁻¹ heating rates under N₂ atmosphere at 20 mL · min⁻¹ flow rate, respectively. The TG runs were repeated at least twice. Evolved gases from TGA were connected to and detected on-line by a FTIR spectrometer. The spectrum scope was located in the range of 400-4000 cm⁻¹. The concentration of each gaseous product was determined based on the integral value of the release curves under specific IR absorptions.

3. Results and Discussions

3.1. TG and DTG curves

Fig.1 presents the weight loss (TG) and the weight-loss rate (DTG) curves for edible mushroom bran at different heating rate. From Fig.1, the pyrolysis of edible mushroom bran shows three stages: the temperature zone of 20~110 °C with a weight loss of 12.33~14.36%, 220~400 °C with a weight loss of 45.09~49.59%, 400~800 °C with a weight loss of 15.11%~ 15.34%, respectively. The total weight loss was around 76%. However, only two DTG peak appears in the three pyrolysis stages. One appears at temperature of 48.2~61.0 °C, another appears at 335.0~349.3 °C at different heating rate. With increasing of heating rate, the TG and DTG curves shift toward higher temperatures. For example, at the second stage with the heating rate of 10 °C min⁻¹, the temperature zone of pyrolysis is 219~383 °C and the maximum weight loss rate corresponding temperature is 335.0 °C; while at the heating rate of 30 °C min⁻¹, the temperature zone of pyrolysis is 221~417 °C and the maximum weight loss rate corresponding temperature is 349.3 °C.

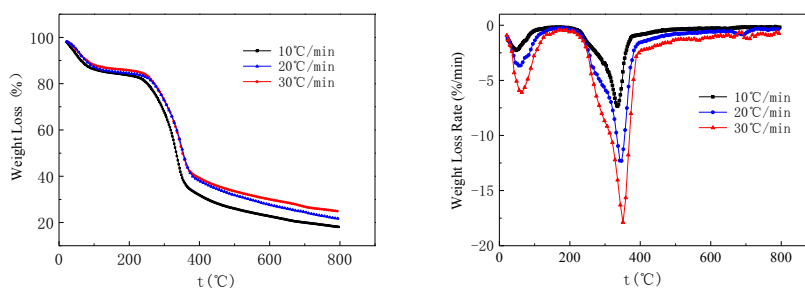


Fig.1 the TG and DTG curves of edible mushroom bran pyrolysis under different heating rates

3.2. FTIR analysis

The pyrolysis gas produced from edible mushroom bran pyrolysis was analysed using the FTIR spectrometer. As for the composition of the pyrolysis vapour, light gases (namely, CO₂, CO, H₂O, CH₄) can be easily detected^[11], whereas some complex compounds such as hydrocarbons, phenols, acids and carbonyl compounds only can be grouped in classes because they are difficult to distinguished in the IR

spectra^[12]. The evolution curves of light gases and complex compounds characterized by FTIR are shown in Fig.2.

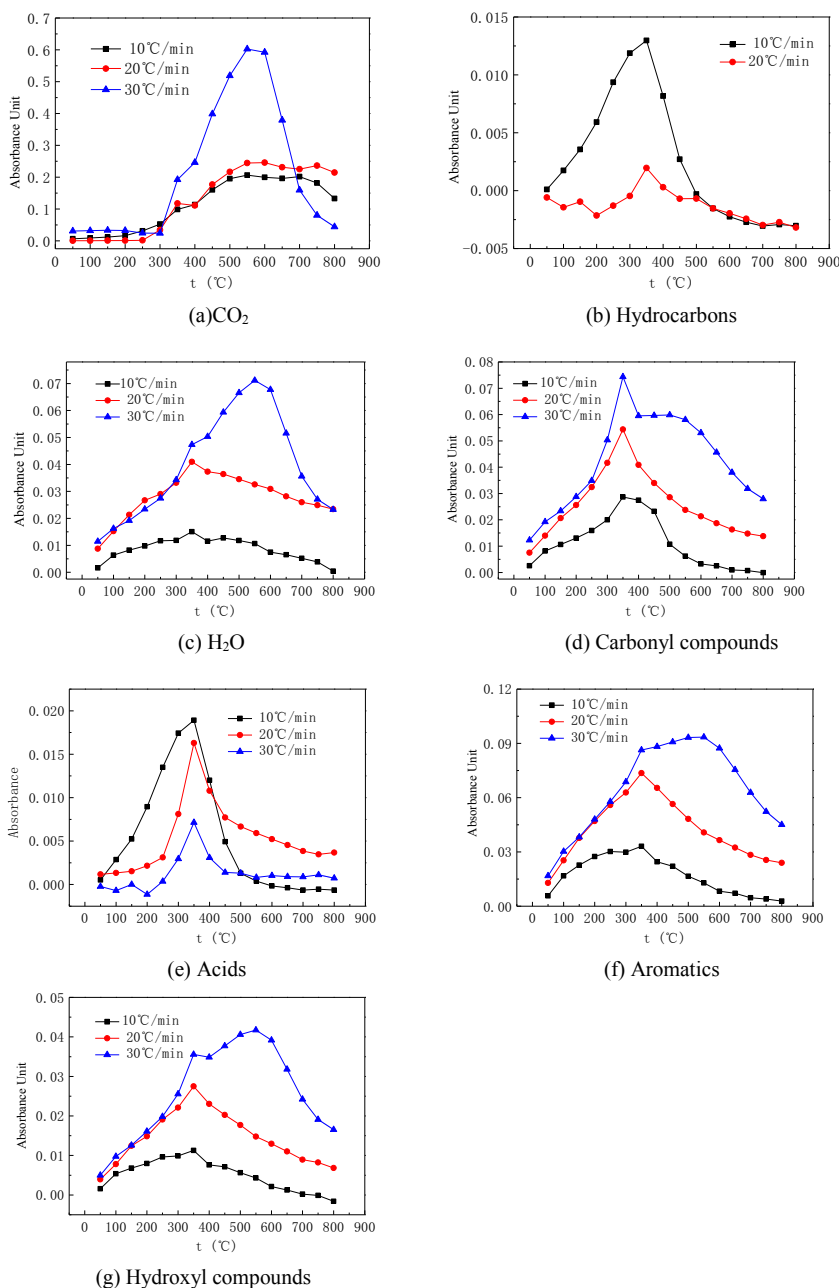



Fig.2 The evolution of the complex volatile species from edible mushroom bran pyrolysis under different heating rate

The assignment of the characteristic wavenumber of the main species of pyrolysis vapour and their maximum occurring temperature are shown in Table 1. Most of the pyrolysis products reach the peak at the temperature of 350°C which is close to the temperature of second maximum weight loss rate (335.0°C at the heating of 10 K/min; 344.0°C at the heating of 20 K/min; 349.3°C at the heating of 30 K/min) of the

DTG curves. Besides, CO_2 reach the peak at the temperature of 550°C . From Fig 2, the heating rates have little effect on maximum occurring temperature of the pyrolysis product for most of the pyrolysis vapour. But, for H_2O , hydroxyl compounds and aromatic, the two peaks appear at the temperature of 350°C and 550°C respectively at the heating rate of 30 K/min while only one peak on 350°C at the heating rate of 10 K/min and 20 K/min occurs.

Table.1 the maximum occurring temperatures of the main volatile products

Wavenumber (cm^{-1})	Assignment	Compounds	$t_{\text{max}} (^\circ\text{C})$		
			$\beta = 10\text{K / min}$	$\beta = 20\text{K / min}$	$\beta = 30\text{K / min}$
3737	O-H stretching	H_2O	350	350	550
3566	O-H stretching	hydroxyl compounds	350	350	550
2968	C-H stretching	Hydrocarbons	350	350	----
2359	C=O stretching	CO_2	550	550	550
1747	C=O stretching	Carbonyl compounds	350	350	350
1509		Aromatic	350	350	550
1063	C-O-H stretching	Acids	350	350	350

Furthermore, it was observed that there have the same evolution curves of aromatics and hydroxyl compounds at the same heating rates. Therefore, it can be deduced that phenol was the main aromatics of the pyrolysis products. The main products of edible mushroom bran were phenols, CO_2 , hydrocarbons, carbonyl compounds, acids.

3.3. Effect of heating rates on compositions of pyrolysis vapor

Literatures^[13] introduce the method of FTIR quantitative analysis technique for pyrolysis gases and the relative concentration of each gaseous product was calculated based on the integral value of the release curves under specific IR absorptions. Fig 3 shows the results. As can be seen from Fig. 3, the yields of H_2O , CO_2 , phenol, and carbonyl compounds add, while the yields of hydrocarbon and acid decrease with the increase of heating rates. The molality of H_2O , CO_2 , phenol, carbonyl compounds at heating rate of 20K/min increase 61.6% , 3.6% , 36.4% , 13.0% compared to that of 10K/min . And the molality of H_2O , CO_2 , phenol, carbonyl compounds at heating rate of 30K/min increase 107.2% , 67.1% ,

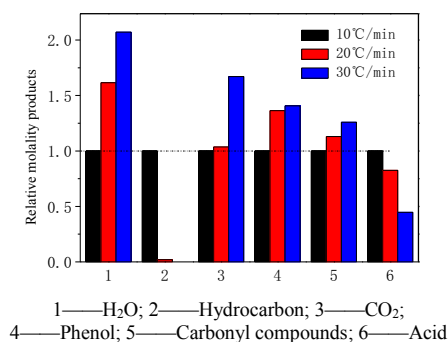


Fig 3. Relative amount of the substance of the main volatile species produced from edible mushroom bran pyrolysis

40.7% , 25.9% compared to that of 10K/min . While molality of acids decrease 17.43% at the heating rate of 20 K/min and 75.30% at the heating rate of 30 K/min compared to that of at the heating rate of 10

K/min. It is noteworthy that molality of hydrocarbon was zero at the heating rate of 30 K/min and a little at the heating rate of 20 K/min compared to that of 10 K/min. These indicate that there is significant influence of heating rates on distribution of pyrolysis vapor composition. At the heating rate of 30K/min, more H₂O, CO₂, phenol, carbonyl compounds and less hydrocarbon and acid were produced.

4. Conclusions

Pyrolysis characteristics and pyrolysis compositions of edible mushroom bran was investigated using TG-FTIR analyser in the temperature range ambient to 800°C under dynamic heating conditions at 10, 20, and 30°C/min heating rates. The effects of heating rates on the molality of pyrolysis vapour were studied. The pyrolysis of edible mushroom bran exhibits three-stage pyrolysis in a temperature range from 20°C to 800°C. The first stage of pyrolysis was from 20 to 100°C, the thermogravimetric loss was 12.33%~14.36%; the second stage pyrolysis was from 220 to 390°C, the thermogravimetric loss was 45.09~49.59%; the second stage pyrolysis was from 380 to 800°C, the thermogravimetric loss was 15.11%~15.34%. With heating rate rising, pyrolysis initial and final temperature, the temperature at the maximum pyrolysis rate increased.

The main pyrolysis vapour of edible mushroom bran was H₂O, hydrocarbon, CO₂, phenol, carbonyl compounds and acids. At the higher heating rate, more H₂O, CO₂, phenol, carbonyl compounds and less hydrocarbon and acid was acquired.

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